Patented May 23, 1939

2,159,012

UNITED STATES PATENT OFFICE

2,159,012

PROCESS FOR ACETYLATING CELLULOSE ACETATE TEXTILE MATERIALS

Henry Dreyfus, London, England

No Drawing. Application September 5, 1935, Serial No. 39,290. In Great Britain September 11, 1934

2 Claims. (Cl. 8—121)

This invention relates to improvements in the production of yarns, fabrics and other materials, and is more particularly concerned with processes for the production of cellulose acetate yarns, fabrics and other materials, and with the new yarns, fabrics and other materials produced thereby.

I have found that the resistance to heat of cellulose acetate yarns, fabrics and other materials may be increased by subjecting the yarns and other materials to acetylation by treatment with diluted acetic anhydride, in the presence of ferric chloride as catalyst. By this means the safe ironing point of the materials may be increased so that they may be ironed without damage at higher temperatures than are customary in ironing ordinary cellulose acetate artificial silk. In addition, the treatment reduces the moisture regain of the materials and they acquire a greater resistance to water and have a substantially greater resistance to the delustring action of hot or boiling aqueous liquids or moist steam. At the same time the tenacity and extension of the materials are well maintained. In addition, the affinity of the yarn for dyestuffs in general, and particularly for the dispersed insoluble dyestuffs now commonly applied to cellulose acetate, is materially reduced, so that by association of the yarns or other materials so treated with yarns or other materials of cellulose acetate or of other organic derivatives of cellulose untreated by the process, differential dyeing effects are obtainable, whilst at the same time the dye has an affinity for the whole of the fabric or other material in which the two types of yarn are associated. Thus, for instance, light and dark blue shades can be produced by the immersion in a dyebath containing an SRA blue dyestuff of a fabric containing ordinary acetone-soluble cellulose acetate yarn together with the same yarn which has been subjected to the process of the invention.

In addition to increasing the resistance to heat and the resistance to water, the new process has the effect of changing the solubility characteristics of the yarns or similar materials. Thus, for instance, by treating cellulose acetate yarn with acetic anhydride according to the present invention, a yarn may be produced which is insoluble or much less soluble in acetone. Similar changes in the solubility characteristics occur in the treatment of other materials used as starting materials in the treatment of the invention. It is thus possible, according to the invention, to produce yarns or other materials which it is difficult or even impossible to manufacture by a simple spinning process.

In the appended claims, the expression "non-solvent liquid medium" is to be understood as meaning a medium which is a non-solvent for the materials being treated throughout the whole of the reaction, and the expression "until products having a reduced solubility in acetone are obtained" is to be understood to include the production of products which are insoluble in acetone.

According to the present invention, therefore, artificial yarns, fabrics and other materials having improved properties are obtained by acetylating such materials having a basis of cellulose acetate by means of acetic anhydride in the presence of ferric chloride.

The invention will hereinafter be described particularly with reference to the acetylation of yarns, but it is to be understood that it is also applicable to fabrics and other materials.

The acetic anhydride is diluted with a diluent which is a non-solvent for the yarn under treatment and is preferably inert thereto, though it may have a swelling action. Good results are obtained with hydrocarbon diluents, for example xylene or other homologues of benzene, tetra- and deca-hydronaphthalenes, and kerosene or other higher boiling petroleum hydrocarbons and also ethers, e. g. normal and iso butyl and amyl ethers, carbon tetrachloride and other non-solvent chlorinated hydrocarbons.

The degree of dilution may be adjusted so as to prevent swelling or so as to obtain some swelling of the yarn. In any case, it should be such as to prevent any solution or incipient solution of the yarn or any fusing together of the filaments, and, further, it may be adjusted to prevent any substantial change in the lustre or quality of the material. A given amount of acetic anhydride may, for example, be dissolved in 7 or 8 or 10 up to 20 times or more of its weight of xylene or other hydrocarbon. The higher dilutions are particularly conducive to avoiding change in the lustre and in quality. The amount of acetic anhydride on the weight of the yarn may vary very considerably, but it is usually sufficient to use an amount of anhydride from half to twice the weight of the material, for example a proportion of 1–1½ times its weight. The proportion may be varied according to the degree of acetylation required and according to the amount of the change in the properties of the material which it is desired to bring about.

The reaction may be carried out under atmospheric pressure, sub-atmospheric pressure, or at pressures in excess of atmospheric, for example pressures of 20 pounds per square inch or more.

The ferric chloride may be employed either alone or in the presence of hydrochloric acid. In general it is found that the presence of hydrochloric acid accelerates the reaction so that the desired degree of further acetylation can be obtained in a shorter time than in the absence of the acid. Preferably hydrochloric acid is introduced into the acetylating medium in the form of

dry gaseous hydrogen chloride. The catalyst is preferably present in the reaction mixture, though it may be present on the yarn before it is brought into contact with the reaction mixture. Where the yarn is previously impregnated with the ferric chloride, it is preferable to apply it in solution and to dry it in the yarn before bringing the yarn into contact with the reaction medium.

The ferric chloride or mixture thereof with hydrochloric acid, is preferably employed in quite low concentrations.

The actual concentration of catalyst will depend upon the concentration of acetic anhydride and other factors. The catalyst should not be employed in a sufficiently high concentration to bring about reaction between the anhydride employed and any diluent if such reaction is possible. For instance, with certain aromatic hydrocarbons acetic anhydride will react in the presence of ferric chloride if present in a sufficiently high concentration.

In general the lower the concentration of the acetic anhydride or catalyst, the longer will the time of treatment be. It may, for example, be 30 minutes or 1 hour up to five hours or more. The conditions necessitating these longer periods of treatment appear to be conducive to greater uniformity of reaction.

For the purpose of brevity, the term "yarn" has been used, but it will be understood that the yarn may be treated in any suitable form, for example in the form of hanks, or on perforated bobbins in the form of woven or warp-knitted or other knitted fabrics or similar materials.

The most important starting material for the purpose of the present invention is cellulose acetate yarn. The starting material may be a yarn produced by the ordinary spinning process, for example the well-known commercial acetone-soluble cellulose acetate yarn, or it may be a yarn treated by any suitable after-treatment process, for example stretching, shrinking, dyeing or other processes. For example, the yarn subsequent to its manufacture may be subjected to a stretching treatment designed to increase its tenacity, for example by means of a solution of dioxane or other suitable solvent or in the presence of steam or hot water, as described in U. S. application S. Nos. 4510 and 4511 filed 1st February 1935. The stretching treatment may, for example, be such as to extend the yarn by 200–500% or even 1000% or more of its original length. Such yarns have an extremely high tenacity which is reflected in the final product, treated according to the present invention. Such stretched yarns, or even ordinary artificial silk materials may, if desired, be subjected to a shrinking treatment to increase their extensibility, for example a shrinking treatment carried out with the aid of latent solvents (see U. S. application S. No. 611,240 filed May 13, 1932, now Patent No. 2,058,422, dated October 27, 1936).

The reaction between the cellulose acetate yarn and the acetic anhydride may be carried out in any suitable manner, for example as a batch process. For example hanks may be immersed for the appropriate period in the acetylation mixture, or the mixture may be pumped or sucked through a perforated bobbin or other package of the yarn.

The following examples are given in order to illustrate the invention, but it is to be understood that they do not limit it in any way. The parts given are by weight in each case.

Example 1

20 parts of acetone-soluble cellulose acetate yarn are treated for about 5 hours at 20–25° C. in a solution consisting of about 450 parts of benzene, 35 parts of acetic anhydride and .7 parts of crystallised ferric chloride. The hanks are then removed, washed first with benzene and then with water and dilute alkali to remove traces of acid and dried.

Example 2

60 parts of acetone-soluble cellulose acetate yarn are treated for about 1 hour at 20–25° C. in a solution consisting of about 1400 parts of benzene, 100 parts of aceticanhydride and 2 parts of crystallised ferric chloride. The yarn is then removed, washed as in the preceding example and dried.

Example 3

60 parts of cellulose acetate yarn are treated for about 18 hours at a temperature of 20–25° C. in a medium consisting of about 800 parts of benzene, 45 parts of acetic anhydride and 1 part of crystallised ferric chloride. The yarn is then removed, washed and dried as in Example 1.

Example 4

60 parts of yarn are treated at a temperature of 20–25° C. for about 1 hour in a medium consisting of about 800 parts of benzene, 100 parts of acetic anhydride, 1 part of crystallised ferric chloride and 4 parts of hydrogen chloride. The yarn is then removed, washed and dried as in Example 1.

The yarn obtained according to each of the preceding examples is chloroform-soluble, has an increased acetyl value, and improved resistance to ironing and to treatment with hot aqueous media and a decreased affinity for the ordinary cellulose acetate dyestuffs.

While the invention has been described above more particularly with reference to yarns, it may also be applied to films, foils and similar materials of cellulose acetate.

What I claim and desire to secure by Letters Patent is:

1. Process for the production of improved artificial materials, which comprises subjecting filaments, yarns, threads and similar textile materials having a basis of acetone-soluble cellulose acetate and fabrics containing such materials to acetylation with a non-solvent liquid medium comprising acetic anhydride, an organic diluent and ferric chloride until products having a reduced solubility in acetone are obtained.

2. Process for the production of improved artificial materials, which comprises subjecting filaments, yarns, threads and similar textile materials having a basis of acetone-soluble cellulose acetate and fabrics containing such materials to acetylation with a non-solvent liquid medium comprising acetic anhydride, an organic diluent, ferric chloride and hydrogen chloride until products having a reduced solubility in acetone are obtained.

HENRY DREYFUS.